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# Appendix A

## **PLANARIZATION FILMS FOR ADVANCED MICROELECTRONIC APPLICATIONS AND DEVICES AND METHODS OF PRODUCTION THEREOF**

This application claims priority to United States Provisional Application Serial Number  
5 60/488484 filed on July 17, 2003.

### **FIELD OF THE SUBJECT MATTER**

The field of the subject matter is planarization compositions and films for use in microelectronic and semiconductor applications, including their methods of production.

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### **BACKGROUND**

To meet the requirements for faster performance, the characteristic dimensions of features of integrated circuit devices have continued to be decreased. Manufacturing of devices with smaller feature sizes introduces new challenges in many of the processes conventionally  
15 used in semiconductor fabrication. One of the challenges of producing microelectronic devices and using them in various applications is the global planarization of a surface having a non-planar surface topography.

Planarization of a surface generally comprises utilizing one or both of two different actions: a) adding to the surface, or b) subtracting from the surface. The action of subtracting  
20 from the surface usually means that the surface is polished or otherwise physically or chemically etched in order to remove any unwanted surface topography and minimize/remove any gaps. The action of adding to the surface usually means adding another layer to the surface topography to fill any gaps and create a smooth surface.

Planarization by addition is not satisfactory where the film thickness measured at the  
25 open field area is substantially greater than that at the surface of the topography. If the film thickness difference between the topography and open field area is too large, a high risk of yield loss at the final device develops. In addition, planarization by addition is not satisfactory or

desirable if the planarization composition cannot adequately fill gaps on the surface, especially the small channels and grooves that are formed on the underlying surface, and in effect leaves small channels that are not filled with planarization composition at all, but are instead filled with air or another atmospheric gas.

- 5           To this end, it would be desirable to form and utilize a planarization composition that can
- a) provide a film thickness that, when measured at the open field area, is not substantially greater than that at the surface of the topography; b) adequately gap fill in narrow trenches and channels;
  - c) be formed using conventional structural and solvent constituents; d) withstand incorporation of other composition-modifying constituents, such as surfactants; and e) planarize a surface or
- 10       substrate to form a component that can be easily incorporated into an electronic or semiconductor application.

### **SUMMARY OF THE SUBJECT MATTER**

5 A planarization composition is disclosed herein that comprises: a) a structural constituent; and b) a solvent system, wherein the solvent system is compatible with the structural constituent and lowers at least one of the intermolecular forces or surface forces components of the planarization composition. A film that includes this planarization composition is also disclosed.

10 In addition, another planarization composition is disclosed herein that comprises: a) a cresol-based polymer compound; and b) a solvent system comprising at least one alcohol and at least one ether acetate-based solvent. A film that includes this planarization composition is also disclosed.

A layered component is also disclosed herein that comprises: a) a substrate having a surface topography; and b) a planarization composition or a film such as those described herein, wherein the composition is coupled to the substrate.

15 Methods of forming a planarization compositions are also disclosed herein that comprise: a) providing a structural constituent; b) providing a solvent system, wherein the solvent system is compatible with the structural constituent and lowers at least one of the intermolecular forces or surface forces components of the planarization composition; and c) blending the structural constituent and the solvent system to form a planarization composition.

20 Methods of forming a film are also disclosed that comprise: a) providing a planarization composition such as those disclosed herein; and b) evaporating at least part of the solvent system to form a film.

### **BRIEF DESCRIPTION OF THE FIGURES**

Figure 1 shows a fluid property comparison for two contemplated planarization compositions.

Figure 2 shows structural information for a contemplated planarization composition.

Figure 3 shows structural information for a contemplated planarization composition.

5 Figure 4 shows planarization performance of a contemplated planarization composition.

Figure 5 shows planarization performance of a contemplated planarization composition.

Figure 6 shows planarization performance of a contemplated planarization composition.

Figure 7 shows planarization performance of a contemplated planarization composition.

Figure 8 shows plasma etch rates of a contemplated planarization composition.

10 Figure 9 shows fill and planarization data for a contemplated planarization composition.

Figure 10 shows fill and planarization data for a contemplated planarization composition.

Figure 11 shows profilometer results for a contemplated planarization composition.

### **DETAILED DESCRIPTION**

As described herein, a planarization composition has been developed and utilized that comprises at least one of the following goals and advantages: a) provides a film thickness that, when measured at the open field area, is not substantially greater than that at the surface of the topography; b) adequately gap fills in narrow trenches and channels; c) is formed using conventional structural and solvent constituents; d) withstands incorporation of other composition-modifying constituents, such as surfactants; and e) planarizes a surface or substrate to form a component that can be easily incorporated into an electronic or semiconductor application.

In contemplated embodiments, a planarization composition comprises a structural constituent and a solvent system, wherein the solvent system is compatible with the structural constituent and effectively lowers at least one of the intermolecular forces or surface forces components of the planarization composition. In additional contemplated embodiments, the planarization composition may further comprise a composition-modifying constituent, such as a surfactant.

The structural constituent of the planarization composition may comprise any suitable monomer, polymer, moiety or compound that is suitable as a planarization material for electronic and semiconductor applications. These monomers, polymers, moieties or compounds can comprise organic, inorganic or organometallic moieties. Examples of contemplated inorganic compounds are silicates, siloxanes, silazanes, aluminates and compounds containing transition metals. Examples of organic compounds include polyarylene ether, polyimides, adamantane molecules, branched adamantane structures, novolac-based polymers and polyesters. Examples of contemplated organometallic compounds include poly(dimethylsiloxane), poly(vinylsiloxane) and poly(trifluoropropylsiloxane).

As used herein, the term "monomer" refers to any chemical compound that is capable of forming a covalent bond with itself or a chemically different compound in a repetitive manner. The repetitive bond formation between monomers may lead to a linear, branched, super-branched, or three-dimensional product. Furthermore, monomers may themselves comprise repetitive building blocks, and when polymerized the polymers formed from such monomers are

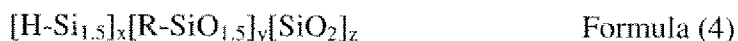
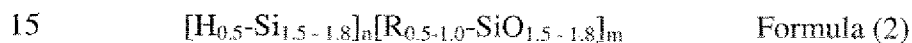
then termed "blockpolymers". Monomers may belong to various chemical classes of molecules including organic, organometallic or inorganic molecules. The molecular weight of monomers may vary greatly between about 40 Dalton and 20000 Dalton. However, especially when monomers comprise repetitive building blocks, monomers may have even higher molecular weights. Monomers may also include additional groups, such as groups used for crosslinking.

One of the planarization compositions that experiences some problems when comparing the film thickness measured at the open field area to that at the surface of the topography is the planarization composition that comprises a novolac-based polymer. Novolac-based polymer solutions contemplated herein are those disclosed in US Issued Patents: 6,506,831; 6,506,441; 6,517,951; US Patent Application Serial No.: 10/299,127 and related and corresponding foreign and PCT applications, including PCT/US99/30296, which are all incorporated herein in their entirety and are commonly owned and assigned to Honeywell International Inc. Other contemplated novolac-based polymer solutions are those disclosed in the following references: Rahman et al. (US 5,853,954 and US 5,910,559); Malik et al. (US 6,027,853); Allen et al. (SPIE Vol. 2438, pp. 250-260); Tsiartas et al. (SPIE Vol. 2438, pp. 261-271) or Sizensky et al (US 5,413,894), which are all incorporated herein by reference. Another class of compositions that are contemplated herein are resol-type phenolic resins. It should be understood that any of the planarization compositions discussed herein may be combined with one another to form another planarization composition. For example, a novolac-based polymer may be combined with a resol-type phenolic resin to form a planarization composition. It should be understood that planarization improves as the structure of the molecular approaches a linear or straight-chained configuration. Branched or crosslinked molecules and compounds can be utilized in a planarization composition, but it should be understood that as the molecules and compounds become larger (from a molecular weight sense) and more complex (from a branched/crosslinked sense) that the successful planarization of a surface may begin to suffer.

Solutions of organohydridosiloxane and organosiloxane resins can also be utilized for forming planarization compositions and also in the fabrication of a variety of electronic devices, micro-electronic devices, particularly semiconductor integrated circuits and various layered materials for electronic and semiconductor components, including hardmask layers, dielectric

layers, etch stop layers and buried etch stop layers. These organohydridosiloxane resin layers are quite compatible with other materials that might be used for layered materials and devices, such as adamantane-based compounds, diamantane-based compounds, silicon-core compounds, organic dielectrics, and nanoporous dielectrics. Compounds that are considerably compatible  
5 with the organohydridosiloxane resin planarization layers contemplated herein are disclosed in PCT Application PCT/US01/32569 filed October 17, 2001; PCT Application PCT/US01/50812 filed December 31, 2001; US Application Serial No. 09/538276; US Application Serial No. 09/544504; US Application Serial No. 09/587851; US Patent 6,214,746; US Patent 6,171,687; US Patent 6,172,128; US Patent 6,156,812, US Application Serial No. 60/350187 filed January  
10 15, 2002; and US 60/347195 filed January 8, 2002, which are all incorporated herein by reference in their entirety.

Organohydridosiloxane resins utilized herein have the following general formulas:



wherein:

20 the sum of n and m, or the sum of x, y and z is from about 8 to about 5000, and m or y is selected such that carbon containing constituents are present in either an amount of less than about 40 percent (Low Organic Content = LOSP) or in an amount greater than about 40 percent (High Organic Content = HOSP); R is selected from substituted and unsubstituted, normal and branched alkyls (methyl, ethyl, butyl, propyl, pentyl), alkenyl groups (vinyl, allyl, isopropenyl),  
25 cycloalkyls, cycloalkenyl groups, aryls (phenyl groups, benzyl groups, naphthalenyl groups, anthracenyl groups and phenanthrenyl groups), and mixtures thereof; and wherein the specific mole percent of carbon containing substituents is a function of the ratio of the amounts of



starting materials. In some LOSP embodiments, particularly favorable results are obtained with the mole percent of carbon containing substituents being in the range of between about 15 mole percent to about 25 mole percent. In some HOSP embodiments, favorable results are obtained with the mole percent of carbon containing substituents are in the range of between about 55  
5 mole percent to about 75 mole percent.

The phrases "cage structure", "cage molecule", and "cage compound" are intended to be used interchangeably and refer to a molecule having at least 10 atoms arranged such that at least one bridge covalently connects two or more atoms of a ring system. In other words, a cage structure, cage molecule or cage compound comprises a plurality of rings formed by covalently  
10 bound atoms, wherein the structure, molecule or compound defines a volume, such that a point located with the volume can not leave the volume without passing through the ring. The bridge and/or the ring system may comprise one or more heteroatoms, and may be aromatic, partially saturated, or unsaturated. Further contemplated cage structures include fullerenes, and crown ethers having at least one bridge. For example, an adamantane or diamantane is considered a  
15 cage structure, while a naphthalene or an aromatic spirocompound are not considered a cage structure under the scope of this definition, because a naphthalene or an aromatic spirocompound do not have one, or more than one bridge.

Contemplated cage compounds need not necessarily be limited to being comprised solely of carbon atoms, but may also include heteroatoms such as N, S, O, P, etc. Heteroatoms may  
20 advantageously introduce non-tetragonal bond angle configurations. With respect to substituents and derivatizations of contemplated cage compounds, it should be recognized that many substituents and derivatizations are appropriate. For example, where the cage compounds are relatively hydrophobic, hydrophilic substituents may be introduced to increase solubility in hydrophilic solvents, or vice versa. Alternatively, in cases where polarity is desired, polar side  
25 groups may be added to the cage compound. It is further contemplated that appropriate substituents may also include thermolabile groups, nucleophilic and electrophilic groups. It should also be appreciated that functional groups may be employed in the cage compound (*e.g.*, to facilitate crosslinking reactions, derivatization reactions, etc.) Where the cage compounds are

derivatized, it is especially contemplated that derivatizations include halogenation of the cage compound, and a particularly preferred halogen is fluorine.

Cage molecules or compounds, as described in detail herein, can also be groups that are attached to a polymer backbone, and therefore, can form nanoporous materials where the cage compound forms one type of void (intramolecular) and where the crosslinking of at least one part of the backbone with itself or another backbone can form another type of void (intermolecular). Additional cage molecules, cage compounds and variations of these molecules and compounds are described in detail in PCT/US01/32569 filed on October 18, 2001, which is herein incorporated by reference in its entirety.

In order to improve the gap-filling and planarization abilities of a composition that comprises monomers or other non-polymer species and/or a polymeric constituent, the composition should be modified in order to modify the viscosity, the surface forces component and/or the intermolecular forces component of the planarization composition, such as the surface energy of the composition. In several cases, it is beneficial to lower both the viscosity and the intermolecular forces constituent in order to optimize the gap-filling and planarization properties. One way to modify the planarization composition is to modify and/or replace the solvent system, wherein the solvent system wherein the system is compatible with the structural constituent and lowers at least one of the intermolecular forces or surface forces components of the planarization composition to which it is added. In some contemplated embodiments, the solvent system comprises at least two solvents.

For example, in a novolac-based polymeric solution, a strongly hydrogen-bonding solvent is used to dissolve the surfactant that is added to the polymeric solution. In one instance, the strongly hydrogen-bonding solvent is ethyl lactate and the surfactant is a fluoroaliphatic polymeric ester surfactant. For this case, the strongly hydrogen-bonding solvent can be replaced by a co-solvent system comprising an alcohol, such as 2-propanol and propylene glycol methyl ether acetate (PGMEA). Utilizing the Hildebrand and Hansen solubility parameters, it is believed that the solubility of fluoroaliphatic polymeric ester surfactant in 2-propanol is similar to that of PGMEA, however, superior to ethyl lactate. In addition, 2-propanol possesses weaker intermolecular forces and lower surface tension than ethyl lactate. The capillary flow in narrow

trenches is affected by the molecular structure and associated electrical charge. Representing integral effects of surface forces, the apparent viscosity of moderately polar 2-propanol decreases from its nominal value at narrow trench regime, where the ratio between apparent and nominal viscosity for ethyl lactate is larger than that of 2-propanol. Addition of PGMEA to 2-propanol in the co-solvent system for the surfactant reduces the evaporation rate difference between 2-propanol and bulk PGMEA used for cresol-novolac resin dilution. In contemplated embodiments, the solvent system lowers the apparent viscosity by at least about 10%. In other contemplated embodiments, the solvent system lowers the apparent viscosity by at least about 20%. In yet other contemplated embodiments, the solvent system lowers the apparent viscosity by at least about 30%.

As used herein, the phrase "apparent viscosity" means the characteristic of fluid's internal resistance to flow and which equals the ratio of stress to the rate of strain. In submicron trenches, the apparent viscosity represents the integral effect of surface forces and usually decreases from the nominal viscosity due to the size effect where the ratio between surface force and body force is large. Also as used herein, the phrase "nominal viscosity" means that viscosity that is the bulk fluid property determined from a commercially available viscometer, such as a Brookfield viscometer, and is calculated from measurements of forces and velocities when liquid is Newtonian.

Contemplated solvents to be utilized in the solvent system are those mentioned earlier along with those that include any suitable pure or mixture of organic molecules that are volatilized at a desired temperature and/or easily solvates the chosen surfactants, polymers and/or other molecules discussed herein. Contemplated solvents are also those solvents that can, alone or in combination, modify the viscosity, intermolecular forces and surface energy of the solution in order to improve the gap-filling and planarization properties. The solvent may also comprise any suitable pure or mixture of polar and non-polar compounds. As used herein, the term "pure" means that component that has a constant composition. For example, pure water is composed solely of  $H_2O$ . As used herein, the term "mixture" means that component that is not pure, including salt water. As used herein, the term "polar" means that characteristic of a molecule or compound that creates an unequal charge, partial charge or spontaneous charge

distribution at one point of or along the molecule or compound. As used herein, the term "non-polar" means that characteristic of a molecule or compound that creates an equal charge, partial charge or spontaneous charge distribution at one point of or along the molecule or compound.

In some contemplated embodiments, the solvent or solvent mixture may comprise those solvents that are not considered part of the hydrocarbon solvent family of compounds, such as ketones, such as acetone, diethyl ketone, methyl ethyl ketone and the like, alcohols (branched and straight chain, such as 2-propanol or 1-propanol), esters, ethers, ether acetates and amines. In yet other contemplated embodiments, the solvent or solvent mixture may comprise a combination of any of the solvents mentioned herein.

In other contemplated embodiments, the solvent or solvent mixture (comprising at least two solvents) comprises those solvents that are considered part of the hydrocarbon family of solvents. Hydrocarbon solvents are those solvents that comprise carbon and hydrogen. It should be understood that a majority of hydrocarbon solvents are non-polar; however, there are a few hydrocarbon solvents that could be considered polar. Hydrocarbon solvents are generally broken down into three classes: aliphatic, cyclic and aromatic. Aliphatic hydrocarbon solvents may comprise both straight-chain compounds and compounds that are branched and possibly crosslinked, however, aliphatic hydrocarbon solvents are not considered cyclic. Cyclic hydrocarbon solvents are those solvents that comprise at least three carbon atoms oriented in a ring structure with properties similar to aliphatic hydrocarbon solvents. Aromatic hydrocarbon solvents are those solvents that comprise generally three or more unsaturated bonds with a single ring or multiple rings attached by a common bond and/or multiple rings fused together. Contemplated hydrocarbon solvents include toluene, xylene, p-xylene, m-xylene, mesitylene, solvent naphtha H, solvent naphtha A, alkanes, such as pentane, hexane, isohexane, heptane, nonane, octane, dodecane, 2-methylbutane, hexadecane, tridecane, pentadecane, cyclopentane, 2,2,4-trimethylpentane, petroleum ethers, halogenated hydrocarbons, such as chlorinated hydrocarbons, nitrated hydrocarbons, benzene, 1,2-dimethylbenzene, 1,2,4-trimethylbenzene, mineral spirits, kerosine, isobutylbenzene, methylnaphthalene, ethyltoluene, ligroine. Particularly contemplated solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene and mixtures or combinations thereof.

As used herein, the phrase "intermolecular forces" means those bonding or non-bonding forces, such as Van der Waals, electrostatic, steric, coulombic, hydrogen bonding, ionic, covalent, dipole-dipole, dispersion, magnetic attraction and combinations thereof, that take place between two or more parts of matter or components, such as a planarization composition and a surface, a planarization composition and another layer of material, molecules that make up the planarization composition, combinations thereof and so on. When lowering the intermolecular forces of a planarization composition, it is important to use a "reference" planarization composition, such as the one described above consisting of a novolac-based polymer, ethyl lactate and a surfactant. When the solvent system of the reference planarization composition is replaced, such as that described above comprising 2-propanol and PGMEA, the intermolecular forces are lowered and the planarization composition is not detrimentally and strongly attracted to the surface of the substrate or to other molecules. In this case, the planarization composition is free to migrate into the narrow gaps and trenches that make up the surface topography. It should be understood that the reference composition may comprise any combination of structural constituents and solvent systems. It should be further understood that whatever reference planarization composition is chosen, a compatible solvent system may be easily developed using the disclosure herein to lower the intermolecular forces component of the composition.

In some embodiments, a surface forces component, such as an interfacial surface tension, is created by the planarization composition and the interaction of the planarization composition with the surface, substrate or wafer. Solvent systems contemplated herein can lower the interfacial surface tension by at least about 10% when compared to a conventional planarization composition known to one of ordinary skill in the art of layered materials. In some embodiments, the solvent system can lower the interfacial surface tension by at least about 20% when compared to a conventional planarization composition. In yet other embodiments, the solvent system can lower the interfacial surface tension by at least about 30% when compared to a conventional planarization composition.

As mentioned earlier, in additional contemplated embodiments, the planarization composition may further comprise at least one composition-modifying constituent, such as a surfactant. Contemplated surfactants include hydrocarbon-based (non-fluorinated) and

fluorocarbon-based surfactants or a combination thereof. As contemplated, the at least one fluorocarbon-type surfactant may comprise at least one fluoroaliphatic polymeric ester surfactant. Suitable non-fluorinated surfactants are those found in US Issued Patents 5,858,547 and 6,517,951 issued to Hacker et al., which are commonly-owned, assigned and incorporated  
5 herein by reference in their entirety. Other composition-modifying constituents may comprise at least one adhesion promoter, pH tuning agent, porogen or any other suitable composition-modifying agent depending on the needs and specifications of the film, the component and/or the vendor.

There are several characteristics of a suitable planarization film that are both desirable  
10 and contemplated herein. A contemplated characteristic of the composition is the polydispersity of the composition. Polydispersity is the ratio of weight-average molecular weight ( $M_w$ ) to number-average molecular weight ( $M_n$ ). Therefore, the closer the weight-average molecular weight is to the number-average molecular weight, the closer the polydispersity is to 1, which is the lowest polydispersity number possible. As polydispersity approaches 1, the constituents in  
15 the composition are closer in molecular weight with little variation in the range of molecular weights in the composition. It has been found that constituents that are not the same or near the same molecular weight as the structural constituent can greatly influence the properties of the film and component incorporating that film. For example, the presence of low-molecular weight constituents in the composition (less than 350 amu) can cause fuming and/or smoking and film  
20 degradation upon baking and curing of the film. In contemplated embodiments, the polydispersity is less than about 3. In other contemplated embodiments, the polydispersity is less than about 2.5. In yet other contemplated embodiments, the polydispersity is less than about 2. And in additional contemplated embodiments, the polydispersity is less than about 1.5.

The planarization compositions described herein may be used to form films. One method  
25 of forming a film comprises: a) providing at least one planarization composition disclosed herein, wherein the planarization composition comprises a solvent system; and b) evaporating at least part of the solvent system to form a film. Any suitable procedure or condition may be used to remove or at least partially remove the solvent system, including continuous sources, such as heat, dissolution in solvents, preferential etching, exposure to radiation, electromagnetic

radiation, such as ultraviolet, x-ray, point sources, such as a laser, or infrared radiation; mechanical energy, such as sonication or physical pressure; or particle radiation, such as gamma ray, alpha particles, neutron beam or electron beam as taught by commonly owned patent publication PCT/US96/08678 and US Patents 6,042,994; 6,080,526; 6,177,143; and 6,235,353, which are commonly owned and incorporated herein by reference in their entireties.

As a contemplated use or application, a layered component is also contemplated herein and comprises: a substrate having a surface topography; a planarization solution and/or film as described herein, wherein the film and/or material is coupled to the substrate; and optionally at least one additional layer of material or film. Contemplated coating materials, coating solutions and films can be utilized are useful in the fabrication of a variety of electronic devices, micro-electronic devices, particularly semiconductor integrated circuits and various layered materials for electronic and semiconductor components, including hardmask layers, dielectric layers, etch stop layers and buried etch stop layers. These coating materials, coating solutions and films are quite compatible with other materials that might be used for layered materials and devices, such as adamantane-based compounds, diamantane-based compounds, silicon-core compounds, organic dielectrics, and nanoporous dielectrics. Compounds that are considerably compatible with the coating materials, coating solutions and films contemplated herein are disclosed in PCT Application PCT/US01/32569 filed October 17, 2001; PCT Application PCT/US01/50812 filed December 31, 2001; US Application Serial No. 09/538276; US Application Serial No. 09/544504; US Application Serial No. 09/587851; US Patent 6,214,746; US Patent 6,171,687; US Patent 6,172,128; US Patent 6,156,812, US Application Serial No. 60/350187 filed January 15, 2002; and US 60/347195 filed January 8, 2002, which are all incorporated herein by reference in their entirety.

Surfaces contemplated herein may comprise any desirable substantially solid material, such as a substrate, wafer or other suitable surface. Some contemplated surfaces comprise a non-planar surface topography and other contemplated surfaces have already been planarized. Particularly desirable substrate layers would comprise films, glass, ceramic, plastic, metal or coated metal, or composite material. Surface and/or substrate layers comprise at least one layer and in some instances comprise a plurality of layers. In preferred embodiments, the substrate

comprises a silicon or germanium arsenide die or wafer surface, a packaging surface such as found in a copper, silver, nickel or gold plated leadframe, a copper surface such as found in a circuit board or package interconnect trace, a via-wall or stiffener interface ("copper" includes considerations of bare copper and its oxides), a polymer-based packaging or board interface such as found in a polyimide-based flex package, lead or other metal alloy solder ball surface, glass and polymers such as polyimide. In more preferred embodiments, the substrate comprises a material common in the integrated circuit industries as well as the packaging and circuit board industries such as silicon, copper, glass, and another polymer. Suitable surfaces contemplated herein may also include another previously formed layered stack, other layered component, or other component altogether. An example of this may be where a dielectric material and CVD barrier layer are first laid down as a layered stack – which is considered the "surface" for the subsequently spun-on layered component.

At least one layer is coupled to the surface or substrate. As used herein, the term "coupled" means that the surface and layer or two layers are physically attached to one another or there's a physical attraction between two parts of matter or components, including bond forces such as covalent and ionic bonding, and non-bond forces such as Van der Waals, electrostatic, coulombic, hydrogen bonding and/or magnetic attraction. Also, as used herein, the term coupled is meant to encompass a situation where the surface and layer or two layers are directly attached to one another, but the term is also meant to encompass the situation where the surface and the layer or plurality of layers are coupled to one another indirectly – such as the case where there's an adhesion promoter layer between the surface and layer or where there's another layer altogether between the surface and layer or plurality of layers.

Contemplated dielectric and low dielectric materials comprise inorganic-based compounds, such as silicon-based disclosed in commonly assigned US Patent 6,143,855 and pending US Serial No. 10/078919 filed February 19, 2002; (for example Honeywell NANOGLASS® and HOSP® products), gallium-based, germanium-based, arsenic-based, boron-based compounds or combinations thereof, and organic-based compounds, such as polyethers, polyarylene ethers disclosed in commonly assigned US Patent 6,124,421 (such as Honeywell FLARE™ product), polyimides, polyesters and adamantane-based or cage-based



compounds disclosed in commonly assigned WO 01/78110 and WO 01/08308 (such as Honeywell GX-3™ product). The dielectric and low dielectric materials may be applied by spin coating the material on to the surface, rolling the material on to the surface, dripping the material on to the surface, and/or spreading the material on to the surface.

5 Nanoporous silica dielectric films with dielectric constants ranging from 1.5 to about 3.8 can be also as at least one of the layers. Nanoporous silica compounds contemplated herein are those compounds found in US Issued Patents: 6,022,812; 6,037,275; 6,042,994; 6,048,804; 6,090,448; 6,126,733; 6,140,254; 6,204,202; 6,208,041; 6,318,124 and 6,319,855. These types of films are laid down as a silicon-based precursor, aged or condensed in the presence of water  
10 and heated sufficiently to remove substantially all of the porogen and to form voids in the film. The silicon-based precursor composition comprises monomers or prepolymers that have the formula:  $R_x-Si-L_y$ , wherein R is independently selected from alkyl groups, aryl groups, hydrogen and combinations thereof, L is an electronegative moiety, such as alkoxy, carboxy, amino, amido, halide, isocyanato and combinations thereof, x is an integer ranging from 0 to  
15 about 2, and y is an integer ranging from about 2 to about 4. Other nanoporous compounds and methods can be found in US Issued Patents 6,156,812; 6,171,687; 6,172,128; 6,214,746; 6,313,185; 6,380,347; and 6,380,270, which are incorporated herein in their entirety.

The layered component contemplated herein may also comprise a diffusion blocking material that is not on the component in the form of a layer, but is instead being used to “block”  
20 any individual pores/voids and not to cover the entire underlying layer. In some embodiments, the diffusion blocking material will react with the underlying low k dielectric material or layer and in other embodiments, The diffusion blocking material will not be reactive with the underlying low k dielectric material or layer. In other embodiments the diffusion blocking layered component contemplated may consist of a densified layer of the low k material or  
25 contain phase separated elements of the low k material densified in such a manner as to block diffusion of species. Diffusion blocking materials, such as those contemplated herein, can be found in commonly-owned US Provisional Application 60/385482 filed on June 3, 2002, which is incorporated herein in its entirety.

Other spin-on materials may be utilized in additional layers of the layered component. Several of the contemplated spin-on materials are described in the following issued patents and pending applications, which are herein incorporated by reference in their entirety: (PCT/US00/15772 filed June 8, 2000; US Application Serial No. 09/330248 filed June 10, 1999; 5 US Application Serial No. 09/491166 filed June 10, 1999; US 6,365,765 issued on April 2, 2002; US 6,268,457 issued on July 31, 2001; US Application Serial No. 10/001143 filed November 10, 2001; US Application Serial No. 09/491166 filed January 26, 2000; PCT/US00/00523 filed January 7, 1999; US 6,177,199 issued January 23, 2001; US 6,358,559 issued March 19, 2002; US 6,218,020 issued April 17, 2001; US 6,361,820 issued March 26, 2002; US 6,218,497 issued 10 April 17, 2001; US 6,359,099 issued March 19, 2002; US 6,143,855 issued November 7, 2000; and US Application Serial No. 09/611528 filed March 20, 1998).

As used herein, the term "metal" means those elements that are in the d-block and f-block of the Periodic Chart of the Elements, along with those elements that have metal-like properties, such as silicon and germanium. As used herein, the phrase "d-block" means those elements that 15 have electrons filling the 3d, 4d, 5d, and 6d orbitals surrounding the nucleus of the element. As used herein, the phrase "f-block" means those elements that have electrons filling the 4f and 5f orbitals surrounding the nucleus of the element, including the lanthanides and the actinides. Preferred metals include indium, silver, copper, aluminum, tin, bismuth, gallium and alloys thereof, silver coated copper, and silver coated aluminum. The term "metal" also includes 20 alloys, metal/metal composites, metal ceramic composites, metal polymer composites, as well as other metal composites. As used herein, the term "compound" means a substance with constant composition that can be broken down into elements by chemical processes.

Additional layers of material may be coupled to the layered component in order to continue building a layered component or printed circuit board. It is contemplated that the 25 additional layers will comprise materials similar to those already described herein, including metals, metal alloys, composite materials, polymers, monomers, organic compounds, inorganic compounds, organometallic compounds, resins, adhesives and optical wave-guide materials.

A layer of laminating material or cladding material can be coupled to the layered interface materials depending on the specifications required by the component. Laminates are

generally considered fiber-reinforced resin dielectric materials. Cladding materials are a subset of laminates that are produced when metals and other materials, such as copper, are incorporated into the laminates. (Harper, Charles A., *Electronic Packaging and Interconnection Handbook*, Second Edition, McGraw-Hill (New York), 1997.)

- 5           Spin-on layers and materials may also be added to the layered interface materials or subsequent layers. Spin-on stacked films are taught by Michael E. Thomas, "Spin-On Stacked Films for Low  $k_{\text{eff}}$  Dielectrics", *Solid State Technology* (July 2001), incorporated herein in its entirety by reference.

10           Examples of other additional layers of materials comprise metals (such as those which might be used to form via fills or printed circuits and also those included in US Patent No. 5,780,755; 6,113,781; 6,348,139 and 6,332,233 all of which are incorporated herein in their entirety), metal diffusion layers, mask layers, anti-reflective coatings layers, adhesion promoter layers and the like.

15           The compounds, coatings, films, materials and the like described herein may be used to become a part of, form part of or form an electronic component and/or semiconductor component. As used herein, the term "electronic component" also means any device or part that can be used in a circuit to obtain some desired electrical action. Electronic components contemplated herein may be classified in many different ways, including classification into active components and passive components. Active components are electronic components  
20           capable of some dynamic function, such as amplification, oscillation, or signal control, which usually requires a power source for its operation. Examples are bipolar transistors, field-effect transistors, and integrated circuits. Passive components are electronic components that are static in operation, i.e., are ordinarily incapable of amplification or oscillation, and usually require no power for their characteristic operation. Examples are conventional resistors, capacitors,  
25           inductors, diodes, rectifiers and fuses.

          Electronic components contemplated herein may also be classified as conductors, semiconductors, or insulators. Here, conductors are components that allow charge carriers (such as electrons) to move with ease among atoms as in an electric current. Examples of conductor components are circuit traces and vias comprising metals. Insulators are components where the

function is substantially related to the ability of a material to be extremely resistant to conduction of current, such as a material employed to electrically separate other components, while semiconductors are components having a function that is substantially related to the ability of a material to conduct current with a natural resistivity between conductors and insulators.

- 5 Examples of semiconductor components are transistors, diodes, some lasers, rectifiers, thyristors and photosensors.

Electronic components contemplated herein may also be classified as power sources or power consumers. Power source components are typically used to power other components, and include batteries, capacitors, coils, and fuel cells. Power consuming components include  
10 resistors, transistors, integrated circuits (ICs), sensors, and the like.

Still further, electronic components contemplated herein may also be classified as discrete or integrated. Discrete components are devices that offer one particular electrical property concentrated at one place in a circuit. Examples are resistors, capacitors, diodes, and transistors. Integrated components are combinations of components that that can provide  
15 multiple electrical properties at one place in a circuit. Examples are integrated circuits in which multiple components and connecting traces are combined to perform multiple or complex functions such as logic.

## **EXAMPLES**

### **EXAMPLE 1**

About 1 gram of fluoroaliphatic polymeric ester surfactant was dissolved at room temperature and pressure in a co-solvent of about 4.5 grams of propylene glycol monomethyl ether acetate (PGMEA) and about 4.5 grams of 2-propanol. About 10 grams of low molecular weight cresol novolac-based resin (MW = about 1500, Mn = 800) was dissolved under ambient conditions in about 15 grams propylene glycol monomethyl ether acetate. A loading of about 5% in weight of such fluoroaliphatic polymeric ester surfactant solution is added to low-molecular weight, low polydispersity cresol novolac-based resin solution and further diluted with about 10 grams of propylene glycol monomethyl ether acetate. This formulated mixture is applied to patterned substrate by spin coating.

Subsequent to propylene glycol monomethyl ether acetate surface-conditioning, the nozzle moves from wafer edge to center and the solution is radially applied to the substrate, which is then spun at gradually increased speeds ranging from about 100 RPM to about 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160°C and about 200°C for about 90 seconds each.

By using these modified polymeric solutions, the thickness difference between the topography and open field area has been significantly reduced and 50% improvement in film planarization property has been achieved.

### **EXAMPLE 2**

About 106.2 g of a low molecular weight (1500 amu) o-cresol novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 7.47 g propylene glycol methyl ether acetate and 7.47g 2-propanol, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500

RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The average film thickness measured was 2.03 micrometers, with a standard deviation of 28 nanometers (0.68% of the average thickness). The resultant coated wafer measured thickness  
5 uniformity with disparity between topography and open area of 600 nanometers at wafer center.

#### **EXAMPLE 3 (COMPARATIVE)**

10 About 106.2 g of a low molecular weight (1500 amu) o-cresol novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 14.9 g ethyl lactate, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The resulting polymeric solution was then dispensed  
15 onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The average film thickness measured was 2.05 micrometers, with a standard deviation of 18 nanometers (0.44% of the average thickness). The resultant coated wafer measured thickness  
20 uniformity with disparity between topography and open area of 1200 nanometer at wafer center.

#### **EXAMPLE 4 (COMPARATIVE)**

25 About 106.2 g of a low molecular weight (1500 amu) o-cresol novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 14.9 g propylene glycol methyl ether acetate, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to  
30 center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated

substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The average film thickness measured was 2.06 micrometers, with a standard deviation of 19 nanometers (0.46% of the average thickness). The resultant coated wafer measured thickness  
5 uniformity with disparity between topography and open area of 750 nanometer at wafer center.

#### **EXAMPLE 5**

10 About 106.2 g of a low molecular weight (950 amu) phenolic novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 7.47 g propylene glycol methyl ether acetate and 7.47g 2-propanol, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution.  
15 The resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The resultant coated wafer measured thickness uniformity with disparity between  
20 topography and open area of 830 nanometers at the wafer center.

#### **EXAMPLE 6 (COMPARATIVE)**

25 About 106.2 g of a low molecular weight (950 amu) phenolic novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 14.9 g ethyl lactate, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The resulting polymeric solution was then dispensed  
30 onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually

increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The resultant coated wafer measured thickness uniformity with disparity between topography and open area of 900 nanometer at wafer center.

5

#### **EXAMPLE 7**

About 106.2 g of a low molecular weight (1300 amu) phenolic novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 7.47 g propylene glycol methyl ether acetate and 7.47g 2-propanol, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

#### **EXAMPLE 7 (COMPARATIVE)**

About 106.2 g of a low molecular weight (1300 amu) phenolic novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 14.9 g ethyl lactate, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

30

The resultant coated wafer measured thickness uniformity with disparity between topography and open area of 900 nanometer at wafer center.



**EXAMPLE 8 (COMPARATIVE TO EXAMPLE 2)**

5 About 106.2 g of a low molecular weight (1500 amu) o-cresol novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 3.32 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 14.9 g propylene glycol methyl ether acetate and 14.9 g 2-propanol, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution.

10 The resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The average film thickness measured was 2.03 micrometers, with a standard deviation of 15 nanometers (0.37% of the average thickness). The resultant coated wafer measured thickness uniformity with disparity between topography and open area of 200 nanometer at wafer center.

**EXAMPLE 9 (COMPARATIVE TO EXAMPLE 2)**

20 About 106.2 g of a low molecular weight (1500 amu) o-cresol novolac polymer was dissolved 159.4 g of propylene glycol methyl ether acetate to yield 265.6 g of a cresol novolac solution. 1.66 g of a fluoroaliphatic polymeric ester surfactant solution with a molecular weight of about 5500 – 8500 amu, and 9.7 g propylene glycol methyl ether acetate and 5 g 2-propanol, was added under ambient conditions to 265.5 g of the cresol novolac polymer solution. The

25 resulting polymeric solution was then dispensed onto an patterned test wafer, was dispensed from wafer edge to center and spun at gradually increased speeds ranging from 100 RPM to 2500 RPM. The coated substrate is placed in two hot plates at a temperature of about 160C and about 200C for about 90 seconds.

The average film thickness measured was 2.1 micrometers, with a standard deviation of 15 nanometers (0.36% of the average thickness). The resultant coated wafer measured thickness uniformity with disparity between topography and open area of 480 nanometer at wafer center.

### **EXAMPLE 10**

Example 10 shows a comparison study between a novolac-based polymer composition, such as those described herein (Accuflo™ 2025) and a second novolac-based polymer composition, also similar to those described herein (Accuflo™ 2027 and/or T2027). Along with the novolac-based polymer (structural constituent), Accuflo™ 2025 comprises 90% PGMEA and 10% ethyl lactate as a solvent system. In addition, along with the novolac-based polymer (structural constituent), Accuflo™ 2027 comprises 92% PGMEA and 8% 2-propanol.

**Figure 1** shows the fluid property comparison from solution for the two compositions at about room temperature (RT) and about 40°C. It can be seen in this Figure that the Accuflo™ 2027 composition reduces the apparent viscosity by about 25% because of the minor composition change in solvent system.

**Figures 2 and 3**, along with **Table 1**, shows the structural information for the composition once the starting composition has been deposited onto a surface or wafer and baked and/or cured. The aging experiments were conducted at about room temperature and at about 40°C. The Cauchy coefficient for Accuflo™ 2027 were calculated when this composition was baked at about 160°C-200°C for about 120 seconds in air. The coefficients that were valid for the wavelength ( $\lambda$ ) range from about 3500Å to about 10,000Å were as follows:

$$\begin{aligned}A(n) &= 1.552 \\B(n) &= 1.76E+6 \text{ Å}^2 \\C(n) &= 1.90E+12 \text{ Å}^4\end{aligned}$$

The refractive index is calculated in the valid wavelength range using the following formula:

$$n(\lambda) = A(n) + B(n) / \lambda^2 + C(n) / \lambda^4$$

The thickness of the Accuflo™ 2027 was about 20347Å. The thickness of the Accuflo™ 2025 in the comparison study was measured to be about 19782Å. In the comparison study, the coefficients that were valid for Accuflo™ 2025 were:

5                       $A(n) = 1.588$   
                          $B(n) = 1.24E+6 \text{ Å}^2$   
                          $C(n) = 2.34E+12 \text{ Å}^4$

10                      **Figures 4 and 5**, along with **Tables 2-7** show the planarization performance for the Accuflo™ 2025 composition tested in two different laboratories. **Figures 6 and 7**, along with **Tables 8-13** show the planarization performance for the Accuflo™ 2027 composition tested in two different laboratories.

15                      **Table 14** shows the TMAH solvent resistance of the Accuflo™ 2027 when baked at about 160°C to about 230°C for about 90 seconds in ambient air. This solvent resistance is identical for all practical purposes to the solvent resistance for Accuflo™ 2025.

**Figure 8** shows that both Accuflo™ 2025 and Accuflo™ 2027 have comparable plasma etch rates. A planarization comparison between the two compositions is shown in **Table 15**.

20                      **Figures 9 and 10** show fill and planarization data collected for the Accuflo™ 2027 composition. **Figure 9** shows the scan path 900, the topography – deep trench arrays 910 and the periphery 920. **Figure 10** shows a schematic of the wafer center 1010 and the wafer edge 1020. Profilometer scan path and two wafer locations were used for this evaluation. Two wafers were used. Analysis of the SEM cross sections were made at three locations: center, mid-wafer and at the edge. **Figure 11** shows the profilometer results. **Table 16** shows the SEM cross  
25                      section results, and **Table 17** shows the BOE etch results for this same composition. Accuflo™ 2027 achieves complete resistance to BOE (500:1) at all bake conditions under study. High bake temperatures of 160°C (100s) - 190°C(100s) - 200°C (210s) is a preferred embodiment to further crosslink polymeric film when concentrated HF etchant is used.

Several conclusions can be drawn from this Example, including the following:

- ✓ With standard spin process, Accuflo™ 2027 presents superior planarization properties as compared to Accuflo™ 2025 because of reduced viscosity and interfacial surface tension.
- ✓ Following process development on Accuflo™ 2025, a contemplated process has been implemented for Accuflo™ 2027 to maximize trench fill property, which comprises gradually increase spin method with and without the radial dispense approach and surface conditioning with PGMEA. Greater than 70% enhancement in local and global planarization has been achieved. The thickness bias between trench arrays and support area have been reduced to 250 nm at wafer center and 150 nm at wafer edge.
- ✓ Bulk film characterization has been conducted on Accuflo™ 2027 and Accuflo™ 2025. Comparable structural (molecular characteristics), physical, process (solvent resistance and plasma etch performance) and optical properties have been observed between the two compositions.
- ✓ Superior global and local planarization in the deep trench arrays/buffer capacitor area can be achieved by application of Accuflo™ 2027 using contemplated spin processes with bake temperatures of about 160°C (about 90 s) – about 220°C (about 90 s) in air ambient. Another optimum bake range is from about 160°C (about 90 s) – about 180°C (about 90 s) in air ambient, which leads to moderate crosslinking, and from about 160°C (about 100 s) – to about 180°C (about 100 s) – to about 200°C (about 210 s) in air ambient, which leads to high crosslinking.

Thus, specific embodiments, methods of formation and applications of modified planarization compositions have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without

departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the disclosure herein. Moreover, in interpreting the specification and claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms “comprises” and “comprising” should be interpreted as referring  
5 to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.